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THE FORMATION AND STUDY OF EXCIPLEX SYSTEMS
A LOW-PRESSURE APPROACH

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DISCLAIMER

I. INTRODUCTION:

The objective of this work is the development of a system for the formation of excimers from their van der Waals ground states. The approach to be taken will use the low temperatures obtained in a free-jet expansion to produce a high steady-state concentration of van der Waals dimer or oligomer. These will be excited by low-energy resonant electron bombardment to yield excimers or exciplexes in an excited vibrotational state. Collisions could, in turn, induce vibrational relaxation of the bound excimer or exciplex. The proposed mechanism is, then, as follows:

$A + B \xrightarrow{1} AB$ (in free jet expansion)

$AB + e^{-1} \xrightarrow{2} AB^{\ddagger} + e^{-1}$ (electron-beam excitation)

$AB^{\ddagger} + M \xrightarrow{3} AB^{*} + M$ (collisional de-excitation)

In the mechanism, A might be a noble gas atom while B could be another noble gas atom, an oxygen atom or a halogen atom. The procedure is based upon the known ability to form dimers and oligomers in the first steps of condensation in a jet expansion. It assumes that excitation by electron-bombardment is a "vertical" process.

The experimental system proposed for these studies is shown schematically in Figure 1. The first quarter of this grant has mainly involved the evolution of design criteria for this system.

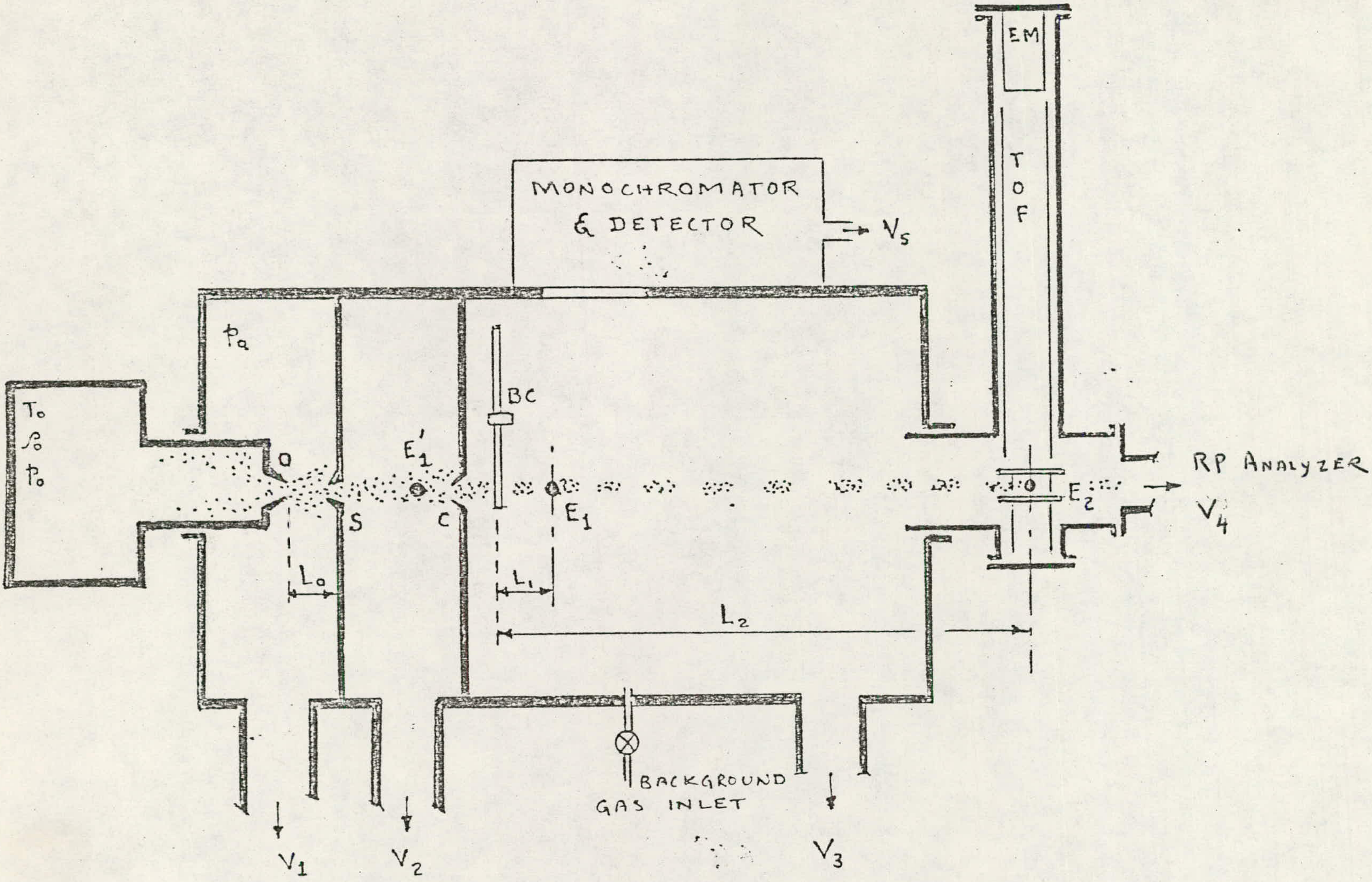

Figure 1. Experimental Apparatus

Orifice O; Skimmer S; Collimator C; Vacuum Pumps V_1, V_2, V_3, V_4, V_5; Beam Chopper BC; Excitation Electron Beam E_1 or E_1'; Analytical Electron Beam E_2; Electron Multiplier EM; Time-of-Flight Mass Analyzer TOF. Note: Distances L_0, L_1 and L_2 are variable.

II: DESIGN OF THE DIMER/OLIGOMER BEAM.

The dimers and oligomers to be studied will be formed in a free jet expansion. A principal part of the instrument design will consequently involve the development of a nozzle-source molecular beam. An in-depth review of the literature has revealed that the technology of cluster beams (beams with condensation nuclei) has lagged that of molecular beams, in general. This has required the derivation of a number of new relations, the validity of which had to be checked against the mass of existing experimental data. Table I includes a summary of design equations which have been developed for a cluster beam.

A number of design criteria have been evolved in terms of the variables in these equations. The most important of these are given in Table II. We are currently designing the nozzle-beam system to meet these criteria and to give optimum dimer intensity. The important experimental variables for controlling dimer concentration will be:

Nozzle-to-skimmer distance,
nozzle diameter,
stagnation pressure, and
stagnation temperature.

Although nozzle shape is an important factor in usual nozzle-beam design, it is unimportant for dimer and lower-oligomer studies. A study of cluster intensity for the various nozzle shapes reported has revealed that intensity increases were due to the

TABLE I: CLUSTER BEAM EQUATIONS

Property	Relation
1. Nozzle Knudsen No.	$K \equiv \frac{\lambda_o}{D}$
2. Skimmer Knudsen No.	$K_{skimmer} \equiv \frac{\lambda_+}{D_{skimmer}}$
3. Mach Disk Knudsen No.	$K_{MD} \equiv \frac{\lambda_+}{D_{MD}}$
4. Nozzle Maximum Mass Flow Rate	$\frac{dm}{dt} = \{\frac{2}{\gamma+1}\}^{\frac{\gamma+1}{2\gamma-2}} \rho_o \frac{\pi D^2}{4} \{\frac{\gamma R T_o}{M}\}^{1/2}$
5. Centerline Jet Density	$\rho = \{\frac{0.0678}{\gamma - 1}\}^{\frac{1}{\gamma-1}} \{\frac{D}{x}\}^2 \rho_o$
6. Location of Mach Disk	$X_{MD} = 0.67\, D\, \{\frac{p_o}{p_+}\}^{1/2}$
7. Location of Virtual Source Point	$x_p = D\, \{0.20\, f - 0.56\}$
8. Mach Number of Flow	$Ma = \frac{5.43}{\gamma} \{\frac{X - X_p}{D}\}^{\gamma-1}$
9. Terminal Mach No.	$Ma_T = 1.17\, K^{-0.4}$
10. Location of Onset of Background Penetration	$X_+ = 0.6\, \frac{D}{K}$
11 Jet Expansion Chamber Background Pressure	$p_+ = \frac{2.86\, p_o\, D^2}{S} \{\frac{T_o}{M}\}^{1/2}$
12. Jet Start-Up-Time	$t_{rise} = \frac{0.0304}{c_o} \frac{X_{BS}}{D_{BS}} D \{\frac{5.43}{\gamma}\}^{5/2} \{\frac{X}{D}\}^{\frac{5(\gamma-1)}{2}}$

TABLE I (Continued)

Property	Relation
13. Jet Decay-Time	$t_{fall} = \frac{X_{skimmer}}{c_+}$

Symbols Used In Table I:

ρ = Density
γ = Heat capacity ratio
λ = Mean free path
c = Speed of Sound

D = Diameter
m = Mass
M = Molar Mass
p = pressure

S = Pumping Speed
T = Kelvin Temperature
X = Distance From Nozzle Exit
f = Thermo degrees of Freedom

Subscripts:

o	denotes stagnation chamber
+	denotes jet-chamber background
BS	denotes properties of jet barrel shock

TABLE II: DESIGN CRITERIA

For jet formation:

$$K \lesssim 0.3$$

For negligible skimmer interference:

$$K_{skimmer} > 50 \quad \text{is} \quad \text{OK.}$$

$$K_{skimmer} < 1 \quad \text{is} \quad \text{OK.}$$

$$1 < K_{skimmer} > 50 \quad \text{is} \quad \text{NoK.}$$

The negligible effect on Jet properties:

$$X_{skimmer} \lesssim \frac{1}{2} X_{MD}$$

For similar cluster intensity and size distribution, two scaling laws have been suggested in the literature:

$$\left\{ p_o \; D^{1/2} \; T_o^{-2.375} \right\} = \text{constant}$$

$$\left\{ p_o \; D \; T_o^{-2.50} \right\} = \text{constant}$$

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formation of beams with larger average cluster size, but that the INTENSITY OF THE DIMERS, TRIMERS AND OTHER LOWER-OLIGOMERS DOES NOT CHANGE WITH NOZZLE SHAPE. This has led us to conclude that a sonic nozzle will be best for the study of the transition from nozzle-beam to cluster-beam flow. More important for our studies, the sonic nozzle will give equally high dimer concentrations without the problem of high concentrations of heavier clusters! We now plan to use precision spinnerette orifices! Another important design decision has been made: If we combine equations 6 and 11 of Table I, we obtain the following interesting result:

$$X_{MD} = 0.40 \quad S^{0.5} \left\{ \frac{M}{T_0} \right\}^{0.25} .$$

The position of the Mach Disk and so all of the geometric properties of the jet are independent of nozzle and chamber properties in a system with a fixed pumping speed! Moreover, to the extent that the fourth-power dependence on T_0 is weak (and so may be neglected), jet geometry will be independent of stagnation conditions as well.

Since the control of jet properties is at the heart of our approach, it is proposed to use a *pulsed* jet expansion. This, in effect, will provide the control of p_+ required in our mechanism. Although this approach adds the mechanical design of a pulsed nozzle to our problems, it will also add another control parameter: the duration of the jet pulse. Equations 12 and 13 have been applied to show steady-state jet expansions can be obtained in times of the order of a millisecond.

III: THE BEAM DETECTION SYSTEM

As part of the dimer/molecular beam apparatus, a modulated-beam mass spectrometer system is being built. The key elements of this system are:

The beam modulation units;
the mass spectrometer;
a retarding potential energy analyzer.

The beam modulation subsystem will be obtained from one of a number of commercial sources. It is considered that this part of the modulated beam spectrometer will pose no significant problems.

A model 12 Bendix Time-of-Flight mass spectrometer has been obtained on a two-year loan from the Environmental Protection Agency, Cincinnati. This unit is planned to be the heart of the modulated-beam system. Considerable time has been spent on the electronics of this unit. If these electronics cannot be made reliable with another month of effort, we will replace them, either with commercial or in-house designed circuits.

Mass spectroscopy of cluster beams is in its infancy. The problem is the lack of any standards for cluster size distributions. The combined use of retarding-potential ion energy analysis and of mass analysis in an alternate-cycle beam monitoring system should provide a new standard for size-distribution measurements. Consequently, an RP analyzer will be added to our apparatus in line with the molecular beam but downstream of the mass spectrometer electron beam. The addition of the RP analyzer represents an improvement over the original proposal which should be very valuable in our study of heteronuclear excimer systems.

IV: PHOTON DETECTION

Principal elements of this component of the apparatus are:

the excitation electron beam,
the photon detectors
the Vac-UV, visible monochromator
the photon-counting system.

Little has been done to date on the design of the excitation electron gun. This unit will be designed in the second quarter of the grant period.

A photon detection system has been designed and ordered. Delivery is expected by the end of March, 1976. Top priority was given to the development of the specifications of this system because it was expected that its components would have the longest delivery times. Basically, the system will include:

Minuteman Laboratories Model
    302-VM Scanning Vac UV-Visible monochromator;
Princeton Applied Research Model
    1109 photon counter;
Principal Applied Research Model
    1121 amplifier-discriminator;
EMI Photomultiplier 9635QB;
Products for Research TE 104 thermoelectric
    refrigerated PM chamber;

Galileo CEM 4000-series channel electron multiplier.

V: CALCULATIONS OF POTENTIAL ENERGY CURVES:

A key assumption in the general application of the low-pressure approach to the study of excimers and exciplexes involves the formation of heteronuclear van der Waals clusters. Little is known of the stability of these species or of the kinetics of their formation and ionization. It is planned to generate ground state potential curves for homo- and heteronuclear noble gas diatomics molecules and ions. These can be used to set theoretical limits on the concentrations of these species which can be formed in the jet expansion and which can be detected mass spectrometrically. The following is a report on other calculations for the Xenon Oxide system.

XENON-OXIDE POTANTIALS

Xenon and oxygen form only weakly bound complexes in the ground and first few excited states, so we decided to calculate the potential curves for ground state xenon interacting with oxygen atoms (in the ^3P, ^1D and ^1S states) using the Gordon-Kim approximation.[1] This treatment neglects electron rearrangement as the atoms approach one another, and permits one to calculate the interaction in terms of the unperturbed atomic electron densities. The interaction is expressed as

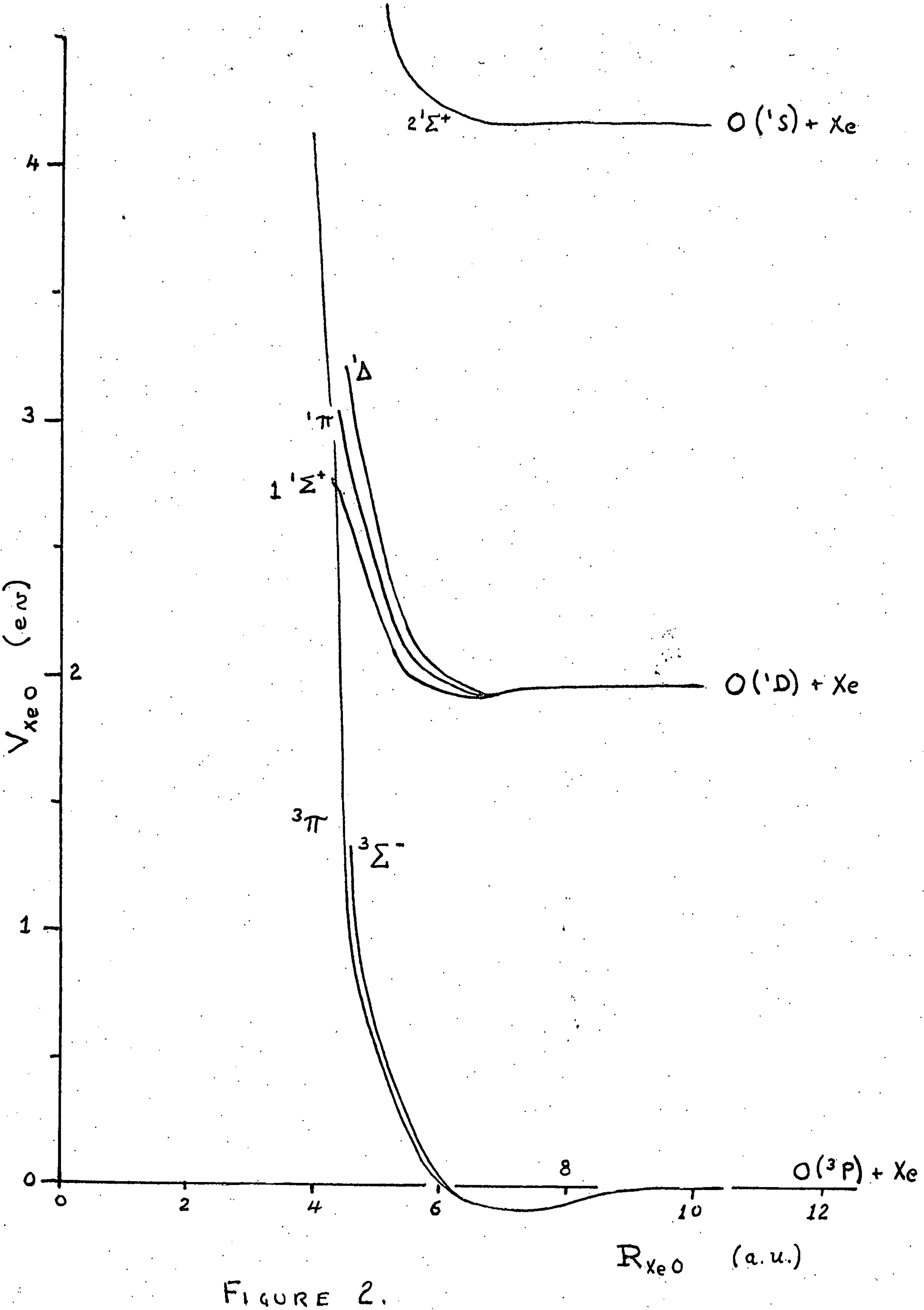
$$V = V_{coul} + V_{gas} ,$$

where the first term includes all Coulombic interactions and the second contains correlation and Hartree-Fock contributions. V_{gas}

is written as an integral of several functions of the electron density which were obtained from the model of a uniform electron gas. This presented no difficulties, and was evaluated in the same manner as done by Kim and Gordon.[1] Evaluation of the Coulombic term required some development because of the non-spherical shape of the oxygen atom's charge density. However, the angular averages could be done analytically, just as Gordon and Kim did for spherical atoms, and the radial integrals were then evaluated by Gauss-Laguerre quadrature.

Using Clementi's SCF wavefunctions[2] for Xe and the three different O states, we obtained the curves shown in Fig. 2 . All curves show weak minima in the neighborhood of 7 a.u. separation. Cooper _et al_[3] and Huestics _et al_[4] have spectroscopically determined some of the well-depths. The latter authors report D_o = 0.324, 0.0275, and 0.0571 eV, respectively, for the $1\,{}^1\Sigma^+$, $1\,{}^1\Pi$, and $2\,{}^1\Sigma^+$ curves. Only the central value is comparable to that found in our calculation. The 0.0571 eV well could result from the addition of polarization effects,[5] but the large value of 0.324 eV probably indicates the importance of some charge-transfer interactions in the $1\,{}^1\Sigma^+$ state, as argued by Huestis _et al._[4]

Our calculations show that the curves arising from $O(^3P)$ do not intersect the $1\,{}^1\Sigma^+$ curve within several kT of its well minimum. If a 0.324 eV well is added to the $1\,{}^1\Sigma^+$ curve, the position of the well is the determining factor in this regard. The position was not determinable from the spectroscopic experiments, however, and its final location will probably have to be found by accurate molecular-orbital calculations.



V_{XeO} (eV)
R_{XeO} (a.u.)
0
1
2
3
4
0
2
4
6
8
10
12
$2\,^1\Sigma^+$
O (^{1}S) + Xe
$^1\Delta$
$^1\Pi$
$1\,^1\Sigma^+$
O (^{1}D) + Xe
$^3\Pi$
$^3\Sigma^-$
O (^{3}P) + Xe

FIGURE 2.

VI: REFERENCES

1. R. G. Gordon and Y. S. Kim, J. Chem. Phys. 56, 3132 (1972).
2. E. Clementi, Atomic Data and Nuclear Data Tables 14, 177 (1974).
3. C. D. Cooper, G. C. Cobb, and E. L. Tolnas, J. Mol. Spectry 7, 223 (1961).
4. D. L. Huestis, ET. AL., Report AD-A009 284, (31 Jan., 1975). NTIS, Dept. of Commerce.
5. Y. S. Kim and R. G. Gordon, J. Chem. Phys. 61, 1 (1974).

VII: PERSONNEL:

The following individuals have constituted the Excimer Study Project Group during the report period.

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